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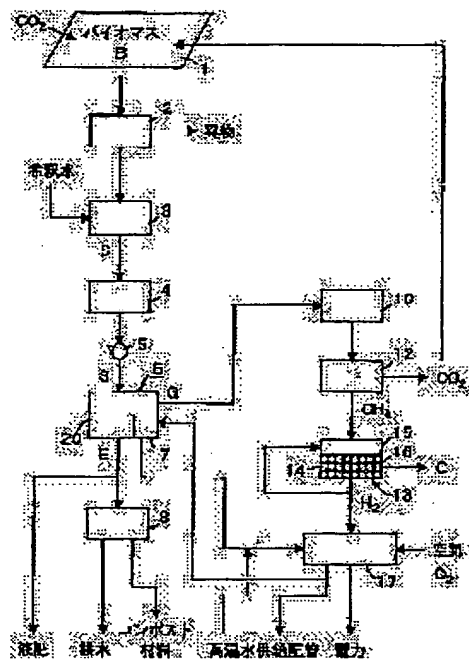
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(54) METHOD AND APPARATUS FOR REMOVING CARBON DIOXIDE BY USING BIOMASS



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method and an apparatus for removing carbon dioxide by using biomass, whereby carbon dioxide can be effectively removed from the atmospheric air in an energetically self-sufficient manner.

SOLUTION: Biomass B in which carbon dioxide in the atmospheric air has been fixed is ground into an organic matter slurry S, the organic slurry S is subjected to methane fermentation by using methanogens kept at the activation temperature. While the methane gas produced by the fermentation is heated to the decomposition temperature, it is decomposed

into hydrogen and solid carbon by contact with a catalyst 14. The carbon dioxide in the atmospheric air is removed in an energetically self-sufficient manner as solid carbon by covering the energy necessary to keep the grinding and activation temperatures and to heat the methane to the decomposition temperature by the combustion energy of the hydrogen. Desirably, the power necessary for the entire system is supported by the system itself by maintaining the methane decomposition reaction by using part of the hydrogen and transforming another part of the hydrogen into electric power and high-temperature water, which keep the temperature of the slurry S, by a fuel battery 17.

[Claim(s)]

[Claim 1]The biomass to which carbon dioxide in the atmosphere was fixed is pulverized to organic matter slurry, Hold said organic matter slurry to active temperature, and methane fermentation is carried out by methane-generating bacteria, Heating methane by said fermentation to decomposition temperature, make a catalyst contact and it decomposes into hydrogen and solid carbon, A carbon-dioxide-removal method of biomass use of removing carbon dioxide in the atmosphere as solid carbon in energy self-sufficiency by providing energy which said grinding, maintenance of active temperature, and heating to decomposition temperature take by energy conversion of said hydrogen.

[Claim 2]In a removing method of claim 1, heating energy to said decomposition temperature is provided with said a part of hydrogen, A carbon-dioxide-removal method

of biomass use of changing said a part of other hydrogen into electric power and high temperature hot water with a fuel cell, providing holding energy of said active temperature with high temperature hot water from said fuel cell, and providing said crushing energy with electric power from said fuel cell.

[Claim 3]A carbon-dioxide-removal method of biomass use which uses said biomass as an organism with high utilization efficiency of carbon dioxide, and grinds this organism in claim 1 or a removing method of 2 to high concentration organic matter slurry with many methane yields per unit weight.

[Claim 4]A carbon-dioxide-removal method of biomass use of using the main ingredients of said catalyst as nickel, iron, or cobalt, heating said methane at 200-900 ** in which removing method of claims 1-3, and making it coming to contact said catalyst.

[Claim 5]A carbon-dioxide-removal method of biomass use which holds said organic matter slurry at 52-58 **, and comes to carry out methane fermentation by methane-generating bacteria in which removing method of claims 1-4.

[Claim 6]A grinding means which pulverizes the biomass to which carbon dioxide in the atmosphere was fixed to organic matter slurry, A bioreactor which has an incubation means which maintains at active temperature of methane-generating bacteria said slurry which took in methane-generating bacteria in a fermentation chamber held at high concentration, and this fermentation chamber, A methane degradation means to have a reaction chamber where a catalyst which disassembles methane from said bioreactor into hydrogen and solid carbon exists, and a heating method which heats said methane from said a part of hydrogen to decomposition temperature, And it has a fuel cell which changes said a part of other hydrogen into electric power and high temperature hot water, A carbon dioxide scrubber compartment of biomass use which drives said grinding means with electric power from said fuel cell and from which said incubation means is kept warm with high temperature hot water from said fuel cell, and carbon dioxide in the atmosphere is removed as solid carbon in energy self-sufficiency.

[Claim 7]A carbon dioxide scrubber compartment of biomass use which uses the main ingredients of said catalyst as nickel, iron, or cobalt, and heats methane at 200-900 ** by said heating method in a stripper of claim 6.

[Claim 8]A carbon dioxide scrubber compartment of biomass use which forms a desulfurization denitrification refiner and a methane concentration device between said bioreactor and a methane degradation means in claim 6 or a stripper of 7.

[Claim 9]A carbon dioxide scrubber compartment of biomass use which pulverizes the biomass by said grinding means in which stripper of claims 6-8 to high concentration organic matter slurry with many methane yields per unit weight.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the method and device from which the inside of the atmosphere or underwater carbon dioxide is removed as solid carbon through a medium of the biomass about the carbon-dioxide-removal method of biomass use, and a device.

[0002]

[Description of the Prior Art] The concentration in the atmosphere is increasing greenhouse gas, such as carbon dioxide (CO₂) leading to global warming, with increase of the fossil fuel amount of consumption after the Industrial Revolution. If the present economic growth was continued without controlling discharge, the CO₂ concentration in the atmosphere has anticipation that it will be come to 700 ppm by 450 ppm and 2100 to being about 360 ppm now in 2030. If the CO₂ concentration in the atmosphere is set to 700 ppm, the mean temperature on the earth carries out an about 2 ** (1-3.5 **) rise, and is considered that unfathomable influence appears in various fields, such as reduction (reduction in a country) of the land by generating of abnormal weather, confusion of an ecosystem and change of production of food, and the rise of the sea level. For this reason, removal of CO₂ in the atmosphere is called for with discharge control of CO₂ for the purpose of reduction of the CO₂ concentration in the atmosphere.

[0003] How to carry out membrane separation out of the air with a poly membrane, ceramic membrane, etc. as a component engineering about removal of CO₂ from the former, The physicochemical methods, such as methods of adsorbing / collecting, such as PSA (Pressure Swing Adsorption), the method of storing in deep sea or underground, the method of absorbing to an organic solvent, and the method of returning to methanol, solid carbon, etc. according to a catalyst, and fixing, are proposed.

[0004] Drawing 6 shows in graph the reduction fixed system to the solid carbon of CO₂ which used natural gas (methane, CH₄) as the reducing agent. In the figure, a catalyst (nickel / SiO₂ catalyst) decomposes CH₄ into solid carbon and hydrogen in the one-step reactor 26 (endoergic reaction), After converting that hydrogen and CO₂ into CH₄ and water (steam) in the two-step reactor 27 (exoergic reaction) and separating this CH₄ from water in the condenser 28, with CH₄ supplied from the outside, it returns to the one-step reactor 26, and reuses as a reducing agent. After all, the reaction of the net in drawing 6 is set to $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{C} + 2\text{H}_2\text{O}$ (following the (3) type).

[0005] JP,2000-271472,A has proposed the CO₂ fixed device using CH₄ generated by aversion processing of an organic waste, as shown in drawing 7. Although the conventional physicochemical CO₂ removing method mainly makes high concentration

CO₂ in a source of release applicable to removal, The CO₂ concentration in the atmosphere is very as thin as about 360 ppm, and in order to remove thin CO₂ efficiently, it needs use of the photosynthetic activity of a living thing, etc. The device of drawing 7 (A) is proposed from such a viewpoint.

[0006]The device of drawing 7 (A) mixes CO₂ in the atmosphere, and the biogas (mixed gas of CH₄ and CO₂) emitted in the organic waste treating part 31 with gas mixture and the condenser 32, Solid carbon and water are generated by causing the reaction of following (1) and (2) type using a catalyst in the reaction vessel 34. The reaction of the net in this case as well as the case of drawing 6 serves as following the (3) type. (2) Although the inversion rate to the solid carbon of CO₂ in a formula is not high, change all CO₂ in gas mixture and the condenser 32 into solid carbon and water by circulating unreacted CO₂ and sending into the reaction vessel 34, as shown in the figure (B). The device aims at improvement in the CO₂ extraction ratio in the atmosphere by fixing CH₄ in biogas, and both of CO₂ and CO₂ in the atmosphere as solid carbon, and controlling the discharge to the exterior of CO₂.

[0007]

[Formula 1]

CH₄→C+2H₂.....(1)CO₂+2H₂→C+2H₂O(2)CH₄+
CO₂→2C+2H₂O(3)[0008]

[Problem(s) to be Solved by the Invention]However, each fixed removal system of CO₂ mentioned above has a problem which must supply energy from the exterior for CO₂ removal. Although the reaction ((3) types) of the net in drawing 6 and drawing 7 is a small exoergic reaction of reaction fever, For example, in the system of drawing 6, consideration of the heat recollection from the two-step reactor 27 and the heat loss in the transfer process to the collected one-step reactor 26 of heat, heat required for reheating of CH₄ separated from water with the condenser 28, etc. will surmise that the heat supply from the outside is indispensable. In the system of drawing 7, the driving power of the organic waste treating part 31, the reaction vessel 34, heat required for heating of catalyst regeneration machine 36 grade, and a system, etc. need to be supplied.

[0009]In order to reduce the energy supply from the outside in the system of drawing 7, The hydrogen eliminator 38 recovers unreacted hydrogen in the reaction vessel 34, a part of collected hydrogen is changed into thermal energy with the hydrogen-burning machine 40, the organic waste treating part 31, the reaction vessel 34, and the catalyst regeneration machine 36 are supplied, and using excessive hydrogen for power generation is proposed (refer to the figure (A)). However, the hydrogen generated by (1)

formula is a substrate required for conversion of CO_2 , and since hydrogen quantity recoverable if there are many amounts of consumption of hydrogen by (2) types decreases, there is a limit in the energy supply and power generation depending on surplus hydrogen. If the hydrogen quantity collected with the hydrogen eliminator 38 is increased, the self-support nature of energy will increase, but since the hydrogen concentration in the reaction vessel 34 falls, there is a possibility of causing decline in the removal efficiency of CO_2 . That is, self-sufficiency of the energy of the whole system is difficult in the system of drawing 7.

[0010]In order to remove CO_2 in the atmosphere, consuming a new fossil fuel should avoid as much as possible, and development of the system from which CO_2 is efficiently removable without the energy supply from the outside is desired. Then, the purpose of this invention is to provide the carbon-dioxide-removal method of biomass use and device from which the carbon dioxide in the atmosphere is removable efficiently and in energy self-sufficiency.

[0011]

[Means for Solving the Problem]An organism which CO_2 in the atmosphere is fixed and this invention person can use as an energy resource. (it is hereafter called the biomass.) -- methane fermentation treatment being carried out, and biogas being generated, and, According to the method which reforms only CH_4 in biogas without CO_2 generation in hydrogen as a result of examining how to reform CH_4 in this biogas in hydrogen. A prospect that difficult SUBJECT that removal of CO_2 in the atmosphere is attained in energy self-sufficiency is solvable was acquired.

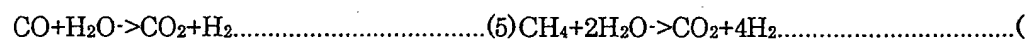
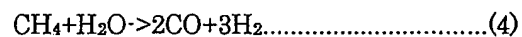
[0012]Vegetation which lives on the earth is fixing CO_2 in the atmosphere to the inside of the body as an organic matter by photosynthesis etc., and carbon based on CO_2 is stored also in the inside of the body of an animal as an organic matter through a food intake of the vegetation, etc. Even when carbon fixed in an organism becomes CO_2 again by combustion etc. and it is spread in the atmosphere, a cause of losing balance of global CO_2 does not become. For this reason, the biomass attracts attention as environmental harmony type alternative energy sources which do not lose balance of global CO_2 even if it burns.

[0013]In a reforming reaction to hydrogen of the conventional CH_4 , a steam is added to CH_4 under an elevated temperature, hydrogen and carbon monoxide (CO) are generated (a steam reforming reaction, (4) types), and also a steam is added to CO and hydrogen and CO_2 are generated (a water gas shift reaction, (5) types). A net reaction becomes like (6) types (this reaction is hereafter called steam reforming). Since H_2O also becomes a source of H_2 at this reaction, there are many amounts of hydrogen generating, but CO_2

occurs simultaneously. This CO₂ does not lose balance of global CO₂, as mentioned above, but it is not preferred from the purpose of CO₂ removal in the atmosphere. [of CO₂ generating in a system] Although it is hard to avoid a byproduction of carbon monoxide (CO) by (4) types in steam reforming, since a catalyst of an electrode will carry out poisoning if CO is mixed with H₂ gas and goes into a fuel cell, it is necessary to remove a priori with a selection contact oxidization method etc.

[0014]

[Formula 2]



[0015] There is the above-mentioned (1) formula as a reaction which carries out direct dissociation of the CH₄ to solid carbon and hydrogen. (1) Since neither CO nor CO₂ is discharged like a steam reforming process according to the formula, hydrogen after decomposition uses it directly as fuel, such as a fuel cell. CO₂ fixed in the biomass is not again diffused in the atmosphere, and it can take out as solid carbon. If CO₂ fixed in the biomass is taken out as solid carbon, the CO₂ concentration in the atmosphere can be reduced as a result.

[0016] With reference to the example of drawing 1, the carbon-dioxide-removal method of biomass use of this invention, The biomass B to which the carbon dioxide in the atmosphere was fixed is pulverized to organic-matter-slurry S, Hold organic-matter-slurry S to active temperature, and methane fermentation is carried out by methane-generating bacteria, Heating methane by fermentation to decomposition temperature, make the catalyst 14 contact and it decomposes into hydrogen and solid carbon, The carbon dioxide in the atmosphere is removed as solid carbon in energy self-sufficiency by providing the energy which said grinding, maintenance of active temperature, and heating to decomposition temperature take by the energy conversion of said hydrogen.

[0017] Preferably, heating energy to said decomposition temperature is provided with said a part of hydrogen, said a part of other hydrogen is changed into electric power and high temperature hot water with the fuel cell 17, holding energy of said active temperature is provided with high temperature hot water from the fuel cell 17, and said crushing energy is provided with electric power from the fuel cell 17. Preferably, the main ingredients of the catalyst 14 are used as nickel, iron, or cobalt, said methane is heated at 200-900 **, and the catalyst 14 is made to contact.

[0018] With reference to an example of drawing 1, a carbon dioxide scrubber compartment of biomass use of this invention, The biomass B to which carbon dioxide in

the atmosphere was fixed. The grinding means 2 and 3 and methane-generating bacteria which are ground to organic-matter-slurry S. The bioreactor 6 which has the incubation means 7 which maintains at active temperature of methane-generating bacteria the slurry S taken in in the fermentation chamber 20 held at high concentration, and the fermentation chamber 20, Methane from the bioreactor 6. It has a methane degradation means 13 to have the reaction chamber 16 where the catalyst 14 decomposed into hydrogen and solid carbon exists, and the heating method 15 which heats methane from said a part of hydrogen to decomposition temperature, and the fuel cell 17 which changes said a part of other hydrogen into electric power and high temperature hot water, The incubation means 7 is kept warm with high temperature hot water from the fuel cell 17, and the grinding means 2 and 3 are driven with electric power from the fuel cell 17, and carbon dioxide in the atmosphere is removed as solid carbon in energy self-sufficiency.

[0019]

[Embodiment of the Invention] In the example of drawing 1, the grinding means 2 and 3 grind the biomass B which raised the plant body as the biomass B and raised it in land or the underwater carbon dioxide (CO_2) fixed institution 1 to high concentration organic matter slurry with many methane (CH_4) yields per unit weight. Although sugarcane on land and corn with high CO_2 utilization efficiency, a soybean, sesame with much oil content of algae seaweed and marine [other] with a quick growth speed, etc. are available as the biomass B, the biomass B used by this invention is not limited to a plant body. many animals and plants which according to this invention live on the earth on condition that it can grind to organic-matter-slurry S -- or -- the -- a part (greenstuff.) The excrement of those processed goods, such as fruits, vegetable oil, fish and shellfishes, and meat, residue (kitchen garbage etc.), and an animal, etc. can be used as the biomass B for CO_2 removal.

[0020] Although the typical things of the organic matter in the biomass B which CO_2 converted are polysaccharide, a fat, protein, etc., if these organic matters are ground to slurry form and methane fermentation is carried out by methane-generating bacteria, with time, it is decomposed gradually and they change to the simple substance. First, polysaccharide changes to monosaccharide and protein changes with the hydrolysis bacilli in methane-generating bacteria to amino acid in the 1st step. Subsequently, these compounds are decomposed into lower fatty acid, such as acetic acid, butanoic acid, and propionic acid, and a small amount of alcohol, aldehyde, etc. by the acid formation bacillus in methane-generating bacteria. Eventually, it becomes a gaseous output which uses CH_4 and CO_2 as the main ingredients by the methane producer in

methane-generating bacteria. This gaseous output is called biogas and contains CO_2 for CH_4 30 to 40% 60 to 70%.

[0021]In order to remove CO_2 in the atmosphere efficiently, it is necessary to collect a lot of possible biogas G from the biomass B efficiently. In order to increase the recovery amount of the biogas G, it is effective to pulverize the biomass B to the slurry form of the diameter of a granule and to grind in particle diameter of 1 mm or less preferably. In the example of drawing 1, the grinder 2 with foreign matter isolation classifies the slurring impossible portion in the biomass B, the portion which can be slurred is broken in a predetermined size, and also the pulverizing mill 3 grinds finely the portion which can be slurred in mean number of about 100 microns. In this invention, since the grinders 2 and 3 are driven by a part of energy conversion of hydrogen from a methane degradation means 13 to mention later, it is not necessary to supply the driving energy for foreign matter separation and grinding from the outside.

[0022]Mobility dilutes the ground slurry S with the water of the quantity which is a grade which becomes good, for example, equivalent weight of water, and it once stores to slurry tank 4 grade. Since dilution-water cost can not only be reducible, but it makes capacity of the bioreactor 6 small and reactor heating energy can be reduced, it is effective to seldom dilute the slurry S but to consider it as high organic substance concentration, when raising the energy self-sufficiency nature of a system. For example, it is the organic substance concentration (a CODcr value, chemical oxygen demand) of the slurry S after dilution 150,000 · 200,000 mg/L (L expresses a liter.) It is below the same. It is considered as the above. Stored organic-matter-slurry S is sent little by little into the bioreactor 6 with the slurry pump 5.

[0023]Since methane fermentation in the bioreactor 6 is performed by an anaerobic condition, its supply of oxygen is unnecessary and there is little energy expenditure. However, the thing for which (1) organic-matter-slurry S is maintained about to pH 6.5 to 8.0 in order for the bioreactor 6 to perform methane fermentation efficiently, (2) Conditions, like maintaining the slurry S to the active temperature of methane-generating bacteria, holding methane-generating bacteria at high concentration in the fermentation chamber 20 of the (3) bioreactor 6, and the blockade by a lot of solid content (SS) contained in the (4) slurry S, etc. do not occur are required.

[0024]There are mesophile which shows activity in a moderate temperature region (35-40 **), and thermophilic bacteria in which activity is shown by a pyrosphere (52-58 **) in methane-generating bacteria. Preferably, it compares with mesophile and necessary biogas is collected for a short time using thermophilic bacteria with quick catabolic rate. In this invention, the slurry S shall be held to the active temperature of

methane-generating bacteria by a part of energy conversion of hydrogen from a methane degradation means 13 to mention later the incubation means 7 formed in the bioreactor 6. An example of the incubation means 7 is a heat exchanger with the slurry S in the high temperature hot water heated by combustion of hydrogen, and the fermentation chamber 20, as shown, for example in the example of drawing 2. The slurry circulating pump 9 shown in drawing 2 can also be driven with a part of electric power by the fuel cell 17 mentioned later, for example.

[0025]Methods of raising the concentration of the methane-generating bacteria in the fermentation chamber 20 include the UASB method (Upflow Anaerobic Sludge Blanket) which granule-izes a microorganism, the fixed-bed method filled up with the carrier to which the microorganism adhered in the fermentation chamber 20, etc. In the fermentation chamber 20 of the bioreactor 6 shown in drawing 2, the hollow cylinder object 22 with an inside diameter of 50-70 mm which has the porosity peripheral wall 23 made of the nonwoven fabric of glass fiber or carbon fiber as shown in drawing 3 is perpendicularly filled up with the microorganism support 21 supported by the frame 24 regularly. By making a methane producer adhere to the carrier 21, the microorganism concentration in the fermentation chamber 20 can be raised. Since it is perpendicularly filled up with the hollow cylinder-like carrier 21 regularly, when the biogas G passes through the inside of the cylindrical carrier 21, the blockade of the carrier 21 by SS etc. can be prevented.

[0026] CH_4 in the biogas G emitted with the bioreactor 6 contains the carbon which constitutes the organic matter in the biomass B, i.e., carbon of CO_2 in the atmosphere. In this invention, the carbon atom of CH_4 in this biogas G is taken out as solid carbon by the methane degradation means 13 (refer to (1) type). From the former, the catalyst which uses as the main ingredients two or more catalysts 14 which decompose CH_4 into solid carbon and hydrogen, for example, nickel, cobalt, iron, etc. is known, and such a catalyst 14 is made to exist in the reaction chamber 16 of the methane degradation means 13 of this invention, and can be used.

[0027]Although illustrated in drawing 1 and drawing 4 as a solid provided with a state, a size, shape, etc. which make the system of reaction a mind-** system and can use the catalyst 14 by a fixed bed reactor by making a reactor into a fixed bed reactor, the system of reaction, a reactor, and a catalyst are not limited to a mind-** system, a fixed bed reactor, and the catalyst for the fixed beds, respectively. The system of reaction may be for example, a mind-liquid-** system. Reactors may be a fluid bed reactor, a moving bed reactor, etc. A fluid and a gas may be sufficient as the state of a catalyst, and pulverized coal, a fine grain, a granular material, byway particles, etc. may be sufficient

as the size of a catalyst, and shape.

[0028]Although the method of putting the catalyst into the reaction chamber beforehand was illustrated as a method of making a catalyst existing in a reaction chamber, in drawing 1 and drawing 4, The method of introducing a catalyst or a catalyst precursor into a reaction chamber together with the CH_4 gas which is a reactant, and the CH_4 gas which is reactants beforehand are put in, and the method of introducing a catalyst or a catalyst precursor there, etc. can be adopted.

[0029]Although a catalyst comprises a main catalyst ingredient, a cocatalyst component, and a carrier and is usually formally called a carried catalyst, the catalyst used by this invention is not limited to a carried catalyst. For example, the catalyst precursor itself is heated in a CH_4 gas atmosphere, and it is activated, and it can be used as a catalyst as it is, or it can blow in into the CH_4 gas which made the catalyst precursor the form of fluids, such as a solution, sol, and a slurry, and heated it, can be activated, and can also be used as a catalyst as it is.

[0030](1) Since the reaction of a formula is an endoergic reaction, it needs to heat CH_4 to the temperature from which a decomposition reaction occurs by the heating method 15. The energy which heating of CH_4 gas takes can be provided with a part of hydrogen generated by the methane degradation means 13. For example, CH_4 is heated even to decomposition temperature by leading a part of hydrogen generated by the methane degradation means 13 to the heating method 15, and burning.

[0031]The main ingredients of the catalyst 14 are used as nickel, cobalt, iron, etc. in the methane degradation means 13 of drawing 4. Although shape of the catalyst 14 is made into spherical (refer to the Drawing (A) and (B)) or the shape of a pyramid (refer to the figure (D)) in the example of a graphic display, the shape of the catalyst 14 is not limited to the example of a graphic display, for example, can adopt various shape, such as cylindrical shape, honeycomb shape, a grain, a swirl, a pellet type, and ring shape. After making carbon generate, the pyramid-like catalyst of the figure (D) is adopted when using as a heat-resistant electromagnetic wave absorber as it is.

[0032] CH_4 is heated at 200-900 **, and the catalyst 14 is made to contact in the example of drawing 4. An inversion rate [in / that temperature is less than 200 ** / a decomposition reaction] (the amount of hydrogen generating) becomes low. If 900 ** is exceeded, a catalyst life will become short, and although an inversion rate does not fall, its final amount of hydrogen generating decreases as a result. this invention person has checked experimentally that hydrogen of the almost same quantity as the theoretical calculation value based on (1) type was generable by heating CH_4 to said decomposition temperature and making the catalyst 14 contact.

[0033]After heating to decomposition temperature, by making the catalyst 14 contact, CH_4 is decomposed even into solid carbon and hydrogen and solid carbon is accumulated on the catalyst 14. Although the crystal structure of the carbon accumulated and shape may change according to the kind of catalyst 14, when it is the nickel catalyst 14, structure of the carbon accumulated can be made into a hollow graphite filament structure useful as high-performance material. Since it will be subdivided and a catalyst will be buried into solid carbon with generation and growth of solid carbon if the catalyst of powder or particle state is used for a longtime reaction, it becomes difficult to separate a catalyst and solid carbon by the usual method. In this case, since a catalyst is widely distributed by a lot of solid carbon, the catalyst content in solid carbon is very low. Depending on a use, it can use effectively as a functional carbon material as it is. On the other hand, a catalyst metallic component is removed from solid carbon by a suitable method and it uses for catalyst regeneration to collect catalysts. The energy which extraction of a catalyst metallic component and reproduction of the catalyst 14 take by this invention can also provide meals by a part of hydrogen generated by the methane degradation means 13.

[0034]The gas which came out from the reaction chamber 16 of the methane degradation means 13 is divided into unreacted CH_4 and hydrogen by suitable methods, such as adsorption and membrane separation. Unreacted CH_4 is returned to the methane degradation means 13. When it burns, it is not only a clean energy source which does not emit CO_2 , but hydrogen has the exothermic energy per unit weight also 3 times of petroleum, and also it can change it into electrical energy with a fuel cell. In this invention, a lot of biogas G is efficiently collected from the biomass B in the grinding means 2 and 3 and the bioreactor 6, By generating hydrogen of the almost same quantity as a theoretical calculation value from CH_4 in the biogas G in the methane degradation means 13, hydrogen of the quantity which can provide all energies required of the inside of grinding, fermentation and decomposition, and other systems can be taken out from the methane degradation means 13. And since CO_2 in the atmosphere fixed in the biomass B is taken out as solid carbon and it does not return into the atmosphere, the CO_2 concentration in the atmosphere can be reduced as a result.

[0035]In this way, offer of "the carbon-dioxide-removal method of biomass use that the carbon dioxide in the atmosphere is removable efficiently and in energy self-sufficiency, and a device" which is the purpose of this invention can be attained.

[0036]

[Example]80 to 90% of organic matters are disassembled by the methane producer

within the bioreactor 6, and organic-matter-slurry S which pulverized the biomass B becomes the biogas G and the fermented mash E. If the elevated-temperature methane fermentation type bioreactor 6 decomposes organic-matter-slurry S whose CODcr value is about 210 g/L, the biogas about 200Nm³ will be emitted per 1 t of slurries. On the other hand, in the example of drawing 1, since a small amount of (10 to 20%) organic matters contain in the fermented mash E which remained in the bioreactor 6, after sending the fermented mash E to the final-treatment institution 8 and purifying it, sewerage and a river have been stocked as treated water. In the final-treatment institution 8, activated sludge treatment using aerobic bacteria, etc. are usually performed. However, it is also possible to use the fermented mash E which remained in the bioreactor 6 as a liquefied fertilizer as it is.

[0037]In the example of drawing 1, the desulfurization denitrification refiner 10 and the methane concentration device 12 are formed between the bioreactor 6 and the methane degradation means 13. Although the biogas G is mainly mixed gas of CH₄ and CO₂, impure substances (tens of ppm - hundreds of ppm), such as hydrogen sulfide and ammonia, are also contained. In order that these impure substances may degrade the catalyst 14 of the methane degradation means 13 or may shorten a life, they are removed in the desulfurization denitrification refiner 10. In the desulfurization denitrification refiner 10 of the example of a graphic display, the biogas G is refined by iron oxide pellets' etc. removing hydrogen sulfide, for example, and removing ammonia with activated carbon etc. The methane concentration device 12 removes CO₂ from the biogas G after refining, and condenses CH₄ to not less than 98%. In the methane concentration device 12 of the example of a graphic display, CH₄ in the biogas G is condensed by carrying out adsorption treatment of the CO₂ with a PSA device.

[0038]CO₂ removed from the biogas G in the methane concentration device 12 can be returned, for example into the atmosphere. CO₂ in the biogas G is CO₂ in the atmosphere originally fixed in the biomass B.

Also when it returns into the atmosphere, balance of global CO₂ is not lost.

Even if it returns into the atmosphere CO₂ contained 30 to 40% in the biogas G, Since CO₂ (carbon conversion) fixed in the biomass B is [more than half] removable if CH₄ contained 60 to 70% in biogas is taken out as solid carbon, it does not become an obstacle of the CO₂ removal in the atmosphere. CO₂ removed from the biogas G can make it able to react to the solid carbon obtained from CH₄, and can also be changed and used for CO which is a chemical raw material.

[0039]In the example of drawing 1, the fuel cell 17 was formed and a part of hydrogen taken out from the methane degradation means 13 is changed into high temperature

hot water and electric power. Although the generation efficiency of the fuel cell 17 is about 40 to 50%, Since high temperature hot water (or steam) is discharged from the fuel cell 17, if this high temperature heat is used effectively, the total energy efficiency of about 80% can be obtained (Kenkichi Hirose "talk of fuel cell" Japanese Standards Association, the July 5, 1992 1st edition, p56). The high temperature hot water which is exhaust heat of the fuel cell 17 is used effective in the incubation means 7 of the bioreactor 6. Electric power required for the drive of the grinding means 2 and 3 shown in drawing 1, the slurry circulating pump 9 (drawing 2) of the bioreactor 6, the final-treatment institution 8, the desulfurization denitrification refiner 10, and methane concentration device 12 grade is provided with a part of electric power from the fuel cell 17.

[0040]In the example of drawing 1, the heating method 15 was heated by a part of hydrogen generated by the methane degradation means 13, and a part of other hydrogen is changed into electric power and high temperature hot water with the fuel cell 17. The high temperature hot water from the fuel cell 17 boils a part at least, the incubation means 7 can be kept warm more, the electric power from the fuel cell 17 can boil a part at least, the grinding means 2 and 3 grades can be driven more, and CO₂ in the atmosphere is removed as solid carbon in energy self-sufficiency.

[0041]One of the antecedent bases judged that this invention is energy self-sufficiency-like is explained with reference to drawing 8. Drawing 8 is a graph which shows the relation of the production of electricity of a system and system power consumption using the above-mentioned methane steam reforming reaction device instead of the methane degradation means 13 in drawing 1 (clean energy (November, 2000), p34-38, Yoshitaka Togo "meta-KURESU and fuel cell"). The production of electricity [graph / alpha / in a figure] according to the throughput of the biomass (drawing 8 kitchen garbage) and the graph beta show change of the power consumption which the drive of a same system takes. According to the graph, the productions of electricity in the case of processing 5 t per of biomasses day are abbreviation 3×10^3 kWh/a day.

It has exceeded the power consumption abbreviation 1×10^3 kWh/the day which the drive of a system takes.

And it turns out that the throughput of the biomass increases and the difference of a production of electricity and this system power consumption spreads.

[0042]When the case where the methane degradation means 13 is used like the case where a methane steam reforming reaction device is used for the hydrogen manufacture from CH₄ like drawing 8, and this invention is compared, clearly like from comparison

with (6) types and (1) type, The amount of hydrogen generating at the time of using the methane degradation means 13 becomes half [at the time of using a methane steam reforming reaction device]. If drawing 8 is seen in consideration of this point, as a production of electricity in the case of processing 5 t per of biomasses day using the methane degradation means 13, abbreviation 1.5×10^3 kWh/a day is expectable.

[0043]On the other hand, if the power consumption which the drive of a system takes is measured, enthalpy change of the reaction at the time of using the case where the methane degradation means 13 is used, and a methane steam reforming reaction device will become almost the same in the reaction temperature of 500 **, and 800 ** per 1 mol of hydrogen. A reaction temperature region also has a field which laps with 200-900 ** in methane degradation, and laps with 600-850 ** in methane steam reforming. Reaction pressure is ordinary pressure and 20 to 30 atmospheres, respectively, and their methane degradation is a little more advantageous (the cited document of the data of methane steam reforming: the Sato trunk group, a PETORO tech, vol.24, and 543 (2001)). It is surmised that the system power consumption at the time of using the methane degradation means 13 like this invention from the above comparison is less than the power consumption (about 1.0×10^3 kWh/a day) at the time of using a methane steam reforming reaction device like drawing 8. That is, when the methane degradation means 13 is used, the surplus electric power about 5.0×10^2 kWh/a day (= $1.5 \times 10^3 - 1.0 \times 10^3$) can be expected, the throughput of the biomass increases and this surplus electric power becomes large. That is, it can be said that this invention is energy self-sufficiency-like.

[0044]Drawing 5 shows one example of the material balance in the case of processing 5 t per of biomasses B to which CO₂ in the atmosphere was fixed day, and energy balance. The 5-t biomass B removes a foreign matter with the grinder 2 with foreign matter isolation before fermentation, pulverizes it with the pulverizing mill 3, and is set to organic-matter-slurry S. In order to improve mobility of the slurry S, 5 t of dilution waters are added and it dilutes twice. The COD_{Cr} value at this time is about 210 g/L, and a BOD value (biological oxygen demand) is about 160 g/L. if methane fermentation is carried out with thermophilic bacteria in the bioreactor 6, keeping this slurry S warm at 55 ** which is the active temperature of thermophilic bacteria, about 85% of COD_{Cr} will be decomposed -- the biogas G -- 1 per day -- it 000 Nm^3 -generates. The average concentration of CH₄ in this biogas G is 65%, and serves as 650 Nm^3 per day as an amount of CH₄. The desulfurization denitrification refiner 10 removes the impure substance in the biogas G, and also CH₄ is condensed to not less than 98% with the methane concentration device 12.

[0045] Condensed CH_4 is supplied to the methane degradation means 13. The reaction chamber 16 of the methane degradation means 13 has the catalyst 14, and is held at the decomposition temperature of 500 **. If CH_4 of $650\text{Nm}^3/\text{day}$ is supplied to the methane degradation means 13, 348 kg per day of carbon and 116 kg of hydrogen can be taken out. The quantity of heat of the taken-out hydrogen is $3,357 \times 10^3 \text{kcal/a}$ day, and let a part of the hydrogen be the fuel of the heating method 15 of the methane degradation means 13. Since $622 \times 10^3 \text{kcal/a}$ day (equivalent to 21 kg-hydrogen / day) is required for making it decompose CH_4 of $650\text{Nm}^3/\text{day}$ at 500 **, the remaining quantity of heat of hydrogen serves as $2,735 \times 10^3 \text{kcal/a}$ day (equivalent to 95 kg-hydrogen / day). Since the generation efficiency of the fuel cell 17 when hydrogen is used as fuel is about 45% when the remainder of this hydrogen is used as the fuel for the phosphoric acid fuel cell 17, the electric power which can be generated serves as 1,431kwh/a day.

[0046] Since the power consumption which the drive of the whole system of drawing 5 takes is 1,000 - 1,200kwh/the degree of schedule, it can cover the power consumption of the whole system enough with the electric power from the fuel cell 17. Since reaction fever is $688 \times 10^3 \text{kcal/a}$ day (equivalent to 24 kg-hydrogen / day) even when decomposition temperature is raised to 800 **, a production of electricity serves as 1,397kwh/a day, and exceeds system power consumption. Since exhaust heat of $1,231 \times 10^3 \text{kcal/a}$ day will arise from the fuel cell 17 if the heat recollection of the about 45% of the reaction fever of hydrogen shall be carried out, it collects as warm water or steam. The quantity of heat which heating to 20 ** to 55 ** of the biomass and a dilution water takes is $350 \times 10^3 \text{kcal/the degree of schedule}$, Since the heat release from the bioreactor 6 is $150 \times 10^3 \text{kcal/the degree of schedule}$, $500 \times 10^3 \text{kcal/the degree of schedule}$ is sufficient for the quantity of heat for keeping the bioreactor 6 warm at 55 **, and it can be enough covered with the warm water from the fuel cell 17.

[0047] From the flow chart of drawing 5, 5 t/day of biomasses B to which CO_2 in the atmosphere was fixed are processed by this invention.

Therefore, 348-kg CO_2 (carbon conversion) is removable as solid carbon.

The energy which removal of CO_2 takes can be altogether provided by the energy conversion of the hydrogen collected within the system, and it is possible to remove CO_2 in energy self-sufficiency. The surplus high temperature hot water about the surplus electric power about 231kwh/a day (=1,431-1,200), $731 \times 10^3 \text{kcal/a}$ day (=1,231 $\times 10^3$ -500 $\times 10^3$) can be made. It is also expectable to obtain the economical efficiency as electric generating facilities, removing CO_2 in the atmosphere.

[0048]

[Effect of the Invention] As explained above, the carbon-dioxide-removal method of

biomass use of this invention, and a device, The biomass to which the carbon dioxide in the atmosphere was fixed is pulverized to organic matter slurry, Holding to active temperature, carrying out methane fermentation by methane-generating bacteria, and heating methane by fermentation to decomposition temperature, make a catalyst contact and it decomposes into hydrogen and solid carbon, Since the energy which said grinding, maintenance of active temperature, and heating to decomposition temperature take is provided by the energy conversion of said hydrogen, the following prominent effect is done so.

[0049](b) Since a system can be driven by using as fuel the hydrogen generated within a system, there is no necessity for the energy supplement from the outside, and the carbon dioxide in the atmosphere can be removed as solid carbon in energy self-sufficiency.

(**) Since the carbon dioxide in the atmosphere is removed through the biomass, the carbon dioxide in the very thin atmosphere is efficiently removable.

(**) If acquisition uses the biomass of an easy kitchen garbage etc., the carbon-dioxide-removal institution in the atmosphere can be built, without choosing a place.

(**) Since the aversion processing with little energy expenditure is used, it is also expectable to stop the energy expenditure in a system to the minimum, and to supply the exterior by making surplus energy into heat and the electrical and electric equipment.

(**) By using the high elevated-temperature methane producer of activity, etc., devices, such as a bioreactor, become compact and are economically advantageous.

(**) By using the catalyst which uses nickel, cobalt, iron, etc. as the main ingredients, solid carbon with structure and shape useful as high-performance material can be taken out, and effective use of solid carbon can be aimed at as the electrode material of a cell, a loss material of an electromagnetic wave absorber, etc.

[Brief Description of the Drawings]

[Drawing 1] It is a diagrammatic flow chart of ** and one example of this invention.

[Drawing 2] It is an explanatory view of the bioreactor in ** and this invention.

[Drawing 3] It is an explanatory view of an example of microorganism support used by ** and this invention.

[Drawing 4] It is an explanatory view of an example of ** and a methane degradation means.

[Drawing 5] It is a figure showing an example of **, the material balance in this invention, and energy balance.

[Drawing 6] It is an explanatory view of an example of the carbon-dioxide-removal method in ** and the conventional atmosphere.

[Drawing 7] It is an explanatory view of other examples of the carbon-dioxide-removal method in ** and the conventional atmosphere.

[Drawing 8] It is an explanatory view of the relation of the production of electricity of a fuel cell and system power consumption which build in ** and the conventional methane steam reforming reaction device.

[Description of Notations]

- 1 -- Carbon-dioxide-fixation-ized institution
- 2 -- Grinder with foreign matter isolation (grinding means)
- 3 -- Pulverizing mill (grinding means)
- 4 -- Slurry tank
- 5 -- Slurry pump 6 -- Bioreactor
- 7 -- Incubation means 8 -- Final-treatment institution
- 9 -- Slurry circulating pump 10 -- Desulfurization denitrification refiner
- 12 -- Methane concentration device 13 -- Methane degradation means
- 14 -- Catalyst 15 -- Heating method
- 16 -- Reaction chamber 17 -- Fuel cell
- 20 -- Fermentation chamber 21 -- Microorganism support
- 22 -- Hollow cylinder object 23 -- Porosity peripheral wall
- 24 -- Frame 26 -- First order reaction machine
- 27 -- Secondary reaction vessel 28 -- Condenser
- 31 -- Organic waste treating part 32 -- Gas mixture and condenser
- 33 -- Pump 34 -- Reaction vessel
- 35 -- Catalyst and carbon eliminator 36 -- Catalyst regeneration machine
- 37 -- Pump 38 -- Hydrogen eliminator
- 39 -- Pump 40 -- Hydrogen-burning machine
- E -- Fermented mash G -- Biogas
- S -- Organic matter slurry

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.